

## PATENT ABSTRACTS OF JAPAN

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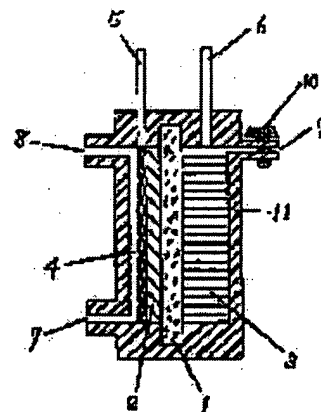
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## (54) ELECTROCHEMICAL CELL AND ACTUATION THEREOF

## (57)Abstract:

**PURPOSE:** To provide a long-life and high-performance electrochemical cell by using fullerenes for active material for one electrode, and using the fullerenes mixed with metal catalyst which effectively acts for dissociation absorption of hydrogen.

**CONSTITUTION:** A cation exchange film 1 acts as electrolyte, and perfluorocarbon sulfonic acid is used. For a positive electrode 2, to active carbon carrying platinum as metal catalyst, dispersion polyethylene tetrafluoride, and mixed solution of Nafion 117 (R) with and water is added to be bound to form an electrode jointed with a Nafion 117 (R) film. For a negative electrode 3, carrying platinum catalyst, dispersion polyethylene tetrafluoride, and mixed solution of the Nafion 117 (R) with alcohol and water are mixed and bound to form an electrode jointed with the Nafion 117 (R) film. An active cap 10 is opened to introduce hydrogen from a hydrogen supply part 9, and after necessary quantity of water is stored in fullerenes, the active cap 10 is closed for usage as a cell.



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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the electrochemistry cel which used cation exchange membrane for the electrolyte.

[0002]

[Description of the Prior Art] There are a fuel cell, a water electrolysis cel, an electrochemical oxygen transfer cel, an electrochemical hydrogen migration cel, etc. as cation exchange membrane and electrochemistry cel using the cation exchange membrane of hydrogen ion conductivity [ detail ] further.

[0003] a fuel cell -- setting -- one side of cation exchange membrane -- the porous electrode as a positive electrode -- on the other hand, it is alike, the porous electrode as a negative electrode is joined to one, respectively, pure oxygen or air is supplied to a positive electrode from the cell exterior, and hydrogen is supplied to a negative electrode from the cell exterior, and is generated by the next reaction.

[0004]

Positive electrode:  $O_2 + 4H^{++} + 4e^- \rightarrow 2H_2O$  (1)

Negative electrode:  $2H_2 \rightarrow 4H^{++} + 4e^-$  (2)

In a water electrolysis cel, a platinum electrode is mainly joined to one by both sides of cation exchange membrane, electrode of the one of the two turns into cathode, the electrode of another side turns into an anode plate, and electrolysis of water takes place by the next reaction.

[0005]

Anode plate:  $2H_2O \rightarrow O_2 + 4H^{++} + 4e^-$  (3)

Cathode:  $4H^{++} + 4e^- \rightarrow 2H_2$  (4)

In the case of a hydrogen migration cel, the negative electrode in an above-mentioned fuel cell and the same electrode turn into an anode plate, and the same cathode as the case of a water electrolysis cel is used. The electrode reaction in this case is as follows.

[0006]

Anode plate:  $H_2 \rightarrow 2H^{++} + 2e^-$  (5)

Cathode:  $2H^{++} + 2e^- \rightarrow H_2$  (6)

That is, the hydrogen supplied to the anode plate serves as a form which moves to cathode from an anode plate.

[0007] Since the supply and circulatory system of a fuel cell of hydrogen are indispensable, generally a fuel cell subsystem becomes intricately and large-scale. One means for solving this point is using a hydrogen storage material for a negative-electrode ingredient. Only oxygen is used depending on the application and a water electrolysis cel has that hydrogen is unnecessary, although hydrogen and oxygen occur by the reaction. Also in this case, if the cathode of an above-mentioned water electrolysis cel is constituted from an electrode which made the hydrogen storage material the subject, the reaction of (1) type will occur in an anode plate, and hydrogen will not occur by the next reaction in cathode.

Cathode:  $xH^{++} + M + xe^- \rightarrow MH_x$  (7)

(M: Hydrogen storage material)

Similarly, if a hydrogen storage material is used for an anode plate in an above-mentioned hydrogen migration cel, the reaction of (8) types will occur and a system will become simple in the semantics that supply of the hydrogen from the cel outside becomes unnecessary.

[0008]

Anode plate:  $MH_x \rightarrow xH^{++} + M + xe^-$  (8)

[0009]

[Problem(s) to be Solved by the Invention] When it joins to the cation exchange membrane which shows strong acid nature as a hydrogen storing metal alloy at one when these hydrogen storage materials are used for the above-mentioned purpose namely, although the LaNi<sub>5</sub>, MmNi<sub>x</sub>Al<sub>y</sub>Mn<sub>z</sub> (Mm: misch metal), and TiNi system etc. is known, generally the corrosion starts and use is actually impossible.

[0010]

[Means for Solving the Problem] The place which it is made in order that this invention may solve the above technical problems in the electrochemistry cel which used cation exchange membrane for the electrolyte, and is made into the purpose is to offer the very long electrochemistry cel of a life.

[0011] The electrode containing the fullerene which supported the metal catalyst which acts effective in the dissociative adsorption of hydrogen instead of the hydrogen storing metal alloy electrode of an electrochemistry cel in this invention, Or the electrode containing the fullerene which supported said catalyst, and the carbon which does not support said catalyst, or the electrode containing the fullerene which supported said catalyst, and the carbon which supported said catalyst, or the electrode containing the fullerene which does not support said catalyst, and the carbon which supported said catalyst is joined, on the other hand, said cation exchange membrane is alike, and the electrode which does not contain fullerene is joined.

[0012]

[Function] The fullerene (Fullerenes) which attracts attention recently is a generic name of the molecule which consists only of carbon expressed with C<sub>60</sub>, C<sub>70</sub>, C<sub>120</sub>, etc. as a molecular formula. These molecules are the polyhedrons for which many regular pentagons formed with carbon and forward hexagons gathered, and among these compounds, C<sub>60</sub> [ most famous ] consists of 12 regular pentagons and 32 forward hexagons, and is called buckminsterfullerene (Buckminsterfullerene) or a buckyball (Buckyball). the inside of that alkali metal (M) dopes between grids and M<sub>3</sub>C<sub>60</sub> (M=K, Rb, etc.) is formed as a fullerene group's chemical property, and the ball of fullerene -- La and calcium -- connoting -- LaC<sub>82</sub> and La<sub>2</sub> -- forming C<sub>82</sub> and CaC<sub>60</sub> -- clear -- \*\*\*\*\*.

[0013] on the other hand -- an invention-in-this-application person etc. -- fullerene -- if independent, physically or electrochemically occlusion of the hydrogen was not carried out, but when carrying out occlusion of the hydrogen if it mixes with carbon other than the fullerene which added the catalyst as generally shows a dissociative-adsorption operation of hydrogen like a platinum metal, or supported these catalysts, and these ingredients constituted the electrode, occlusion of the hydrogen was carried out electrochemically, and it discovered \*\*\*\*\*ing. And fullerene found out that strong corrosion resistance was shown to cation exchange membrane. This invention is made based on such discovery.

[0014] Although this invention is applicable to above-mentioned various electrochemistry cels, the electrode containing fullerene consists of mixture with the binder like Pori ethylene tetrafluoride in the mixture of the thing and fullerene which supported the catalyst like platinum to the thing which supported the catalyst like platinum with the usual approach to fullerene, or activated carbon which is used for the usual fuel cell, and is conventionally joined to the cation exchange membrane which is the electrolyte of the proton conductivity in a well-known approach by one. moreover, the time of joining the electrode containing this fullerene to cation exchange membrane -- the inside of an electrode -- or it is effective that you mix the mixed solution of the organic solvent of cation exchange resin and water in the plane of composition of an electrode and the film, respectively, or make it placed between it.

[0015] What makes a perfluorocarbon or styrene-divinylbenzene copolymer a frame and has a sulfonic acid group or a carboxylic-acid radical as an ion exchange group as cation exchange membrane is effective.

[0016] In the case of a fuel cell, when a fullerene electrode is conventionally used for a positive electrode at a negative electrode using a well-known oxygen electrode or an air electrode, an oxygen (air)-fullerene cell is constituted. The occlusion of the hydrogen to a fullerene electrode may be the back before constituting an electrode. A hydrogen feed hopper is prepared in a cell, making a fuel cell subsystem into a sealing system, and making it a primary-cell type which will be discarded if the hydrogen in fullerene is consumed by discharge can also supply hydrogen intermittently from the cell outside, and it can also discharge repeatedly. If it does in this way, it is complicated and very convenient practically at the point of ending even if size does not always attach the \*\*\*\*\* circulatory system to a cell. Supply of the hydrogen to a fullerene electrode moreover, as an oxygen electrode (positive electrode) For example, constitute from an ingredient which makes a subject the carbon which supported the platinum catalyst, and an electrode which functions also as the so-called hydrogen electrode is used. If hydrogen is supplied from the cell exterior and it energizes between this positive electrode and a fullerene electrode (negative electrode) instead of supplying oxygen or air to this positive electrode, occlusion of the hydrogen will be electrochemically carried out to a fullerene electrode by the next reaction.

[0017] Positive electrode (it operates as an anode plate in fact) :  $x/2$ , and  $H_2 \rightarrow xH^{++} + xe^-$  -negative electrode (it operates as cathode in fact):  $CF_1 + xH^{++} + xe^- \rightarrow CF_1 + HX$  ( $CF_1$ : fullerene)

Although this reaction is irregular, it can be called a kind of charge. (9) The cell electrical potential difference at the time of charge by the formula and (10) types is advantageous at the point of being very low.

[0018] If a fullerene electrode is used for the cathode of a water electrolysis cell instead of a hydrogen generating electrode, hydrogen generating from cathode will be prevented and only the oxygen evolution from an anode plate will happen. Such a cell did not exist at all conventionally. This became possible for the first time by application of a fullerene electrode which has corrosion resistance to cation exchange membrane. In the semantics that the electrolysis reaction of water occurs in an anode plate, although such an electrochemistry cell can be called water electrolysis cell, it should differ in effect like before the so-called water electrolysis cell which oxygen and hydrogen generate, and a little, and should call it an electrochemical oxygen evolution cell rather. This oxygen evolution cell is very useful for an application for which high-concentration oxygen on site is needed instead of an oxygen cylinder, for example, medical application.

[0019] Therefore, the hydrogen migration cell which arranged the fullerene electrode on the anode plate and allotted the hydrogen generating electrode to cathode can obtain hydrogen always anywhere to the energization to this electrochemistry cell, if occlusion of the hydrogen is beforehand carried out to the fullerene electrode. Moreover, although platinum which therefore deposits on the surface of cation exchange membrane is consisted of by the hydrogen generating electrode in this case at the so-called electroless deposition method While making it the gas diffusion electrode which can ionize hydrogen gas, making this gas diffusion electrode into an anode plate like the case of the above-mentioned fuel cell and using an above-mentioned fullerene electrode as cathode If a direct current is energized between two electrodes, supplying hydrogen to a gas diffusion electrode, the same reaction as the above-mentioned (9) types and (10) types occurs, occlusion of the hydrogen is carried out to a fullerene electrode, and it can be used as a repeat hydrogen generating cell. An electrochemistry cell with such a function does not have the former, either, and starts this invention person's etc. invention.

[0020]

[Example] Hereafter, the example of this invention is explained.

[0021] the porous carbon electrode which supported the platinum as a positive electrode was joined to one side of [example 1] cation exchange membrane, and the fuel cell which joined and constituted the electrode containing the fullerene which was alike on the other hand and supported the platinum catalyst as a negative electrode was produced. Drawing 1 was what showed the cross-section structure, and in drawing, 1 is \*\*\*\*\* cation exchange membrane as an electrolyte, and used perfluorocarbon sulfonic acid (trade name: Nafion 117) with a diameter [ of 50mm ], and a thickness of about 0.2mm here. To the activated carbon which 2 is a positive electrode and supported the platinum as a metal catalyst 2%, dispersion poly ethylene tetrafluoride, The mixed solution of the alcohol of Nafion 117 and water is added and bound. The electrode joined to Nafion 117 film and 3 are negative electrodes, and are the electrode which added and bound the mixed solution of the fullerene C60 which supported 10% of platinum catalyst, dispersion poly ethylene tetrafluoride, and the alcohol of Nafion 117 and water, and was joined to Nafion 117 film. In addition, the magnitude of an electrode made the positive electrode and the negative electrode the diameter of 40mm. 4 -- the titanium network as a positive-electrode charge collector, and 5 -- for a gas inlet and 8, as for a hydrogen feed hopper and 10, a gas outlet and 9 are [ a positive-electrode terminal and 6 / a negative-electrode terminal and 7 / a stopper cock and 11 ] cell cases. In addition, in assembling a cell, hydrogen hardly exists in fullerene C60. In using this fuel cell, it is necessary to carry out occlusion of the hydrogen into the fullerene of a negative electrode first. The one approach is an approach contact direct hydrogen to fullerene and it carries out occlusion to it, and after opening a stopper cock 10, introducing hydrogen from the hydrogen feed hopper 9 and carrying out occlusion of the hydrogen of an initial complement to fullerene, it closes a stopper cock 10 and it is used for it as a cell. the case where a 100mA direct current is energized in the direction in which another approach is an electrochemical process, hydrogen is supplied to the gas inlet 6 of a positive electrode, and an electron moves to a negative electrode from a positive electrode through an external circuit at coincidence -- a positive electrode -- the reaction of (9) types -- moreover, in a negative electrode, the reaction of (10) types occurs and occlusion of the hydrogen is electrochemically carried out into the fullerene C60 of a negative electrode. This process is a kind of charge, and the hydrogen feed hopper 9 and stopper cock 10 of drawing 1 are unnecessary as structure of a cell.

[0022] Next, if oxygen is supplied to the gas inlet 6 of a positive electrode and a load is connected between a positive electrode and a negative electrode, with a positive electrode, the reaction of (1) type occurs, with a negative electrode, the next reaction (11) occurs and a 50mA current can be taken out electrical-potential-difference 0.8V.

[0023]

Negative electrode:  $\text{CF}_1, \text{HX} \rightarrow \text{CF}_1 + \text{xH}^+ + \text{x e}^-$  (11)

( $\text{CF}_1$  fullerene)

The capacity of this fuel cell is determined in the fullerene of a negative electrode in the amount of the hydrogen by which occlusion is carried out. Of course, the same property is acquired also when air is supplied to the gas inlet 6 of a positive electrode instead of oxygen [an example 2]. The material of construction and structures other than a negative electrode produced the completely same fuel cell as an example 1. As a negative electrode, \*\*\*\* and fullerene C60 which support the platinum catalyst 2% to the very large carbon of surface area beforehand instead of, and supported the platinum catalyst were mixed, the mixed solution of dispersion poly ethylene tetrafluoride, and the alcohol of Nafion 117 and water was added and bound, and the electrode joined to Nafion 117 film was used. [ the fullerene which supported the platinum catalyst ] The property of this fuel cell was almost the same as the example 1. [0024] [example 3] The platinum electrode as an anode plate was joined to one side of cation exchange membrane, and the water electrolysis cel which joined and constituted the electrode containing the fullerene which was alike on the other hand and supported 10% of platinum catalyst as cathode was produced. Drawing 2 was what showed the cross-section structure, and in drawing, 1 is \*\*\*\*\* cation exchange membrane as an electrolyte, and used perfluorocarbon sulfonic acid (trade name: Nafion 117) with a diameter [ of 50mm ], and a thickness of about 0.2mm here. 2 is an anode plate, and the platinum electrode joined by the electroless deposition method and 3 are cathode, and are the electrode which added and bound the mixed solution of the fullerene C60 which supported 10% of platinum catalyst, dispersion poly ethylene tetrafluoride, and the alcohol of Nafion 117 and water, and was joined to Nafion 117 film. In addition, the magnitude of an electrode made an anode plate and cathode the diameter of 40mm. As for the water with which an anode terminal is electrolyzed for 4 and a cathode terminal and 6 are electrolyzed for 5, and 7, a gas outlet and 8 are cel cases. In addition, in assembling a cel, hydrogen hardly exists in fullerene C60. [0025] When a 100mA [ per cel ] direct current is energized from an external circuit in this water electrolysis cel, The hydrogen ion which the reaction of (3) types occurred in the anode plate, water decomposed, and about 23ml of oxygen of 25 degrees C per hour and one atmospheric pressure occurred from the gas outlet 9, and was made into \*\*\*\*\* coincidence Reaching a cathode side through Nafion 117 film, the reaction of (10) types occurs, occlusion is carried out into fullerene C60, and gas does not occur from cathode in cathode. This water electrolysis cel can be called electrochemical oxygen evolution cel.

[Example 4] The material of construction and structures other than cathode produced the completely same water electrolysis cel as an example 3. As cathode, the carbon and fullerene C60 which support the platinum catalyst 2% to the very large carbon of surface area beforehand instead of, and supported the platinum catalyst were mixed, the mixed solution of dispersion poly ethylene tetrafluoride, and the alcohol of Nafion 117 and water was added and bound, and the electrode joined to Nafion 117 film was used. [ the fullerene which supported the platinum catalyst ] The property of this water electrolysis cel was almost the same as the example 3.

[0026] [Example 5] Drawing 3 which produced the hydrogen migration cel of structure similar to the fuel cell stated in the example 1 was what showed the cross-section structure, and in drawing, 1 is \*\*\*\*\* cation exchange membrane as an electrolyte, and used perfluorocarbon sulfonic acid (trade name: Nafion 117) with a diameter [ of 50mm ], and a thickness of about 0.2mm here. To the activated carbon which 2 is cathode and supported the platinum as a metal catalyst 2%, dispersion poly ethylene tetrafluoride, The mixed solution of the alcohol of Nafion 117 and water is added and bound. The mixture of the fullerene C60 and C70 which the electrode joined to Nafion 117 film and 3 are anode plates, and supported 10% of platinum catalyst, It is the electrode which added and bound the mixed solution of dispersion poly ethylene tetrafluoride, and the alcohol of Nafion 117 and water, and was joined to Nafion 117 film. In addition, the magnitude of an electrode made cathode and an anode plate the diameter of 40mm. For an anode terminal and 6, as for a hydrogen feed hopper and 8, a hydrogen gas outlet and 7 are [ 4 / a cathode terminal and 5 / a stopper cock and 9 ] cel cases. In addition, in assembling a cel, hydrogen hardly exists in fullerene.

[0027] In using this hydrogen migration cel, it is necessary to carry out occlusion of the hydrogen into the fullerene of an anode plate first. The one approach is an approach contact direct hydrogen to fullerene and it carries out occlusion to it, and after opening a stopper cock 8, introducing hydrogen from the hydrogen feed hopper 7 and carrying out occlusion of the hydrogen of an initial complement to fullerene, it closes a stopper cock 8 and it is used for it as a hydrogen migration cel. Another approach is an electrochemical process and supplies hydrogen to the gas inlet 6 of cathode 2 (in this case, it operates as an anode plate). In the direction in which an electron moves to an anode plate 3 (in this case, it operates as cathode) from cathode 2 through an external circuit at coincidence the case where a 100mA direct current is energized -- cathode 2 -- the reaction of (9) types -- moreover, in an anode plate 3, the reaction of (10) types occurs and occlusion of the hydrogen is electrochemically carried out into the fullerene (mixture of C60 and C70) of an anode plate. As structure of a cel, the hydrogen feed hopper 7 and stopper cock 8 of

drawing 3 are unnecessary.

[0028] Next, when a 50mA [ per cel ] direct current is energized from an external circuit, in an anode plate 3, the reaction of (11) types occurs, the hydrogen in fullerene dissociates into a hydrogen ion and an electron, a hydrogen ion reaches a cathode 2 side through Nafion 117 film, the reaction of (6) types occurs and hydrogen gas generates it in cathode 2. This hydrogen migration cel can be called electrochemical hydrogen generating cel.

[0029] In addition, although it is also possible to use the porous platinum electrode joined by the electroless deposition method as cathode 2, as an approach of carrying out occlusion of the hydrogen to fullerene, it is restricted to the approach of contacting direct hydrogen to fullerene, and an electrochemical process cannot be used in this case.

[0030] [Example 6] The material of construction and structures other than an anode plate produced the completely same hydrogen migration cel as an example 5. As an anode plate, the carbon and fullerene C60 which support the platinum catalyst 2% to the very large carbon of surface area beforehand instead of, and supported the platinum catalyst were mixed, the mixed solution of dispersion poly ethylene tetrafluoride, and the alcohol of Nafion 117 and water was added and bound, and the electrode joined to Nafion 117 film was used. [ the fullerene which supported the platinum catalyst ] The property of this hydrogen migration cel was almost the same as the example 5.

[0031]

[Effect of the Invention] The electrochemistry cel which becomes this invention uses fullerene for the active material of one electrode, and mixes and uses the metal catalyst which acts effective in the dissociative adsorption of hydrogen for fullerene. That is, although occlusion of the hydrogen is not carried out at all only by fullerene making hydrogen merely contact, by mixing a catalyst like platinum to fullerene comes to show the capacity which carries out occlusion of the hydrogen electrochemically. Although the device is not clear, hydrogen once sticks to a catalyst, a hydrogen content child dissociates to a hydrogen atom, and a device which carries out occlusion of the after hydrogen atom is presumed.

[0032] Thus, in the electrode containing the fullerene of the electrochemistry cel which becomes this invention, since fullerene consists of only carbon and the solid-state macromolecule ionic conductor of strong acid nature like Nafion 117 does not receive corrosion, the very long electrochemistry cel of a cycle life is obtained.

[0033] If the electrochemistry cel which becomes this invention is used for a fuel cell, therefore, only by supplying oxygen or air to a positive electrode If supply of the gas by the side of a negative electrode becomes unnecessary, and structure becomes easy and it uses for a water electrolysis cel Only oxygen is generated, hydrogen serves as oxygen generators which do not come out outside at all, and further, if it uses for a hydrogen migration cel, a hydrogen gas storage container will serve as unnecessary dehydrogenation equipment in a well-closed container, or a hydrogen generator.

[0034] Moreover, although the synthetic approach is difficult and is the expensive matter, since fullerene is matter which consists only of carbon, if it comes to be produced in large quantities at present, possibility of becoming cheap is large and the natural worries like a resource are completely unnecessary.

[0035] In addition, as fullerene, it is also possible to use the fullerene from which molecular weight, such as C70, differs besides C60 stated in the example, and, of course, use of the mixture of two or more kinds of fullerene is also possible. Moreover, as a metal catalyst which acts effective in the dissociative adsorption of hydrogen, use of many metals, such as palladium and nickel, is also possible besides the platinum stated in the example. Moreover, use of the carbon of various classes, such as activated carbon with large surface area, is possible also for the class of carbon which supports a catalyst. Furthermore, as the quality of the material of a porous electrode, use of various ingredients, such as a solid-state macromolecule ionic conductor, and various metals, carbon powder which does not react, is possible besides the platinum stated in the example.

[0036] as mentioned above, the electrochemistry cel of a life which becomes this invention is very long -- moreover -- a resource -- carrying out -- very abundant carbon can be used, the trouble of the conventional electrochemistry cel can be removed, and the industrial value is very large.

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[Translation done.]